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Electrical conductivity; oriented polyacetylene; polycrystalline films of $(CH)_x$; transport properties; electrical anisotropy; temperature dependence of $\sigma_{\parallel}$; dopant concentrations; semiconductor-to-metal transition; quasi-one-dimensional metal; electronic properties; four-probe techniques; stretched $(CH)_x$ films; scanning electron microscope pictures; randomly oriented $(CH)_x$ (over)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Partial orientation of the fibers in polycrystalline films of $(CH)_x$ leads to significant improvement in the transport properties and to the introduction of electrical anisotropy. With an elongation $\ell/\ell_0 \sim 3$, the room temperature conductivity of AsF_5 doped $(CH)_x$ is in excess of 2000 $(\Omega\text{-cm})^{-1}$, i.e. comparable to that of high quality single crystals of $(SN)_x$. From studies of the temperature dependence we conclude that the intrinsic $\sigma_{\parallel}$ appropriate to the fully oriented polymer is considerably higher. The increase in anisotropy on doping suggests that at dopant concentrations above the semiconductor-to-metal (over)

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film; inter-fibril contact; charge-transfer model; acceptors; polycation; polymer chains; $[CH(AsF_5)_{0.10}]_x$; $[CHI_{0.25}]_x$.

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transition, the metallic state may be quasi-one-dimensional.

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ANISOTROPIC ELECTRICAL CONDUCTIVITY OF PARTIALLY ORIENTED POLYACETYLENE[*]

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Abstract

Partial orientation of the fibers in polycrystalline films of $(CH)_x$ leads to significant improvement in the transport properties and to the introduction of electrical anisotropy. With an elongation $\ell/\ell_o \simeq 3$, the room temperature conductivity of AsF_5 doped $(CH)_x$ is in excess of $2000 \ (\Omega\text{-cm})^{-1}$, i.e. comparable to that of high quality single crystals of $(SN)_x$. From studies of the temperature dependence we conclude that the intrinsic $\sigma_\parallel$ appropriate to the fully oriented polymer is considerably higher. The increase in anisotropy on doping suggests that at dopant concentrations above the semiconductor-to-metal transition, the metallic state may be quasi-one-dimensional.

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In a series of recent studies,[1-5] we have demonstrated that the
semiconducting polymer $(CH)_x$, polyacetylene, can be chemically doped[1-4]
with donors or acceptors to yield n-type or p-type material,[5] that the two
kinds of dopants can compensate one another,[5] and that a p-n junction can
be formed.[5] Through careful control of the dopant concentration,[1-5] we have
shown that the electrical conductivity can be systematically varied over
eleven orders of magnitude covering the full range from insulator to
semiconductor to metal. Transport and infrared transmission studies
indicate a semiconductor-to-metal transition at a dopant concentration
near 1%.[2] The room temperature electrical conductivity of as-grown
polycrystalline films of cis-$[CH(AsF_6)_{0.14}]_x$ was reported as 560 $(\Omega\text{-cm})^{-1}$;[2]
comparable to the best single crystals of organic metals such as TTF-TCNQ.[6]

This high conductivity is particularly interesting since electron
microscopy studies[7] show that the $(CH)_x$ films consist of tangled randomly
oriented fibrils (typical fibril diameter of a few hundred angstroms). The
measured density[8] is 0.4 gm/cm³ compared with 1.2 gm/cm³ as obtained by
flotation techniques, indicating that the polymer fibrils fill only about one-
third of the total volume. X-ray studies[7,8] show that the $(CH)_x$ films are poly-
crystalline with interchain spacing of approximately 3.8 Å. Consequently we
expect the interchain electronic transfer integrals to be small, ~ 0.1 eV, i.e.,
less than or comparable to the intermolecular transfer integrals along the

b-axis in TTF-TCNQ[6] where the intermolecular spacing is 3.6 Å. On the other hand, molecular spectroscopic studies of short chain polymers lead to the conclusion that the intrachain transfer integrals for carbon atoms separated by ~1.4 Å are of order 2 - 2.5 eV.[9] Thus we anticipate a highly anisotropic band structure with correspondingly anisotropic transport in $(CH)_x$. Indirect evidence of this was obtained from the temperature dependence of the conductivity in $(CH)_x$ doped to concentrations above the semiconductor-to-metal transition.[2] The conductivity was found to decrease on lowering the temperature in a manner similar to that observed in polycrystalline $(SN)_x$,[10] sublimed films of $(SN)_x$[11] or polycrystalline TTF-TCNQ[12] where the transport is limited by a combination of anisotropy and interparticle contact. In these cases, the conductivity decreases even though the single crystal transport measurements along the principal conducting axis clearly imply metallic behavior.

Shirakawa and Ikeda have recently reported[13] significant orientation of $(CH)_x$ after stretch elongation; they have been able to vary the amount of orientation by combined mechanical and thermal treatment resulting in elongation with $l/l_o \sim 1$ to 3 where l is the final stretched length and l_o is the unstretched length.

In this paper we present a survey of our initial studies of the electronic properties of these partially oriented $(CH)_x$ films. We find

that the orientation results in electrical anisotropy with $\sigma_{\parallel}/\sigma_{\perp} \simeq 10$ in the undoped films ($\parallel$ and $\perp$ refer to parallel and perpendicular to the orientation direction). The electrical anisotropy increases with doping suggesting quasi-one-dimensional metallic behavior in the fully oriented doped polymer. For stretched $[CH(AsF_5)_{0.10}]_x$ with $\ell/\ell_0 \simeq 3$, $\sigma_{\parallel}(300 \text{ K}) >$ 2000 $(\Omega\text{-cm})^{-1}$ with anisotropy of approximately 16. The temperature dependence of the conductivity in the doped oriented films indicates that the conducting polymer remains metallic to low temperatures.

The polymer films were synthesized using techniques developed by Shirakawa et al.[7] and described in earlier publications. Orientation was achieved by stretching cis-$(CH)_x$ films at room temperature with subsequent additional stretching during isomerization at 200°C. Details on the orientation techniques are presented elsewhere.[13] The electrical conductivity was measured by four-probe techniques using samples cut parallel and perpendicular to the orientation direction. The results were supplemented and independently checked by means of measurements using the method developed by Montgomery[14] which yields the anisotropy and the parallel and perpendicular conductivities directly from a single sample. After initial measurement, the samples were doped with iodine or AsF_5 and subsequently measured both at room temperature and as a function of temperature. Dopant concentrations were determined from weight increase. Typical samples for 4-probe measurement were films 1 cm

by $\frac{1}{2}$ cm with a thickness of 0.1 mm. The Electrodag contacts were painted across the width of the sample. The Montgomery samples had similar dimensions and thus were well in the thin sample limit; Electrodag contacts were painted on the four corners.

The room temperature results are summarized in Figure 1. The anisotropy is plotted in Fig. 1a as a function of dopant concentration for $l/l_o = 2.30$ and $l/l_o = 2.91$. The induced anisotropy of the undoped oriented films appears to increase approximately as the square of the elongation (prior to stretching the non-aligned samples are isotropic both before and after doping with AsF_5). The anisotropy remains after doping, increasing modestly with iodine and more steeply with AsF_5. The effects of elongation (alignment) on the absolute values of $\sigma_{||}$ and $\sigma_{\perp}$ are shown on Fig. 1b for the heavily doped metallic polymer $[CH(AsF_5)_{0.10}]_x$. The parallel conductivity increases dramatically with alignment; the solid curve follows $\sigma = \sigma_o (l/l_o)^2$ where $\sigma_o = 300 \ \Omega^{-1}$-$cm^{-1}$.

Scanning electron microscope pictures of the films as grown and after stretch alignment are shown in Fig. 2. The characteristic branched and twisted fibrils of the unstretched polymer discussed earlier by Shirakawa et al.[7] are clearly visible in Fig. 2a. Elongation results in alignment as shown in Fig. 2b. However comparison of the two shows that the fractional alignment is modest. Detailed experiments to provide a quantitative measure of the fractional alignment are in progress.

The temperature dependences of the parallel and perpendicular conductivities and the anisotropy for an oriented film ($l/l_o = 2.91$) doped

into the metallic regime with AsF_5 are shown in Figure 3. The solid points result from four probe measurements on two separate ($\parallel$ and $\perp$) films; the x points result from the Montgomery measurements. The three samples were taken from the same initial film and doped simultaneously to a final composition $[CH(AsF_5)_{0.10}]_x$. We expect the Montgomery technique to give the most reliable data since the measurements were taken on a single sample. The four-probe data come from two separate samples ($\parallel$ and $\perp$), so that slightly different final compositions are possible. Nevertheless, the results from the two independent sets of measurements are consistent, and the general agreement is excellent. The room temperature parallel conductivity is in excess of 2000 $(\Omega\text{-cm})^{-1}$; the average of the two measurements yields 2150 $(\Omega\text{-cm})^{-1}$. On cooling, $\sigma_{\parallel}$ and $\sigma_{\perp}$ decrease slowly; however, the conductivity remains high even at the lowest temperatures consistent with metallic behavior. A more detailed examination of the data shows that $\sigma_{\parallel}$ remains approximately constant, increasing slightly ($\sim 0.5\%$) down to 260 K, whereas $\sigma_{\perp}$ decreases monotonically.

The results of these initial studies on oriented $(CH)_x$ must be compared with earlier results on the random polymer.[1-5] The general conclusion is that the transport is indeed limited by a combination of interparticle contact and anisotropy even in the partially oriented films.

The intrinsic conductivity along the $(CH)_x$ chain direction in the doped metallic polymer may be much higher than the measured value. The trends in the data together with the electron microscope photographs suggest that better orientation will lead to considerable enhancement of the anisotropy and the absolute room temperature conductivity (Fig. 1) with $\sigma_{\parallel}(T)$ probably increasing substantially on cooling.

The dependence of the induced anisotropy on elongation as implied in Figure 1 can be understood on a geometrical basis. Stretching increases the number of parallel fibers per unit cross section along the stretch direction and allows current to flow longer distances in this direction without the necessity of transport across the inter-fibril contact. However, the number of fibrils running perpendicular per unit cross section is correspondingly reduced so that the perpendicular transport remains dominated by inter-fibril contacts. The resulting anisotropy and parallel conductivity therefore increases dramatically in agreement with Figure 1.

The observed increase in anisotropy after doping is consistent with the charge-transfer model[4,5] developed for the doping mechanism in polyacetylene. The acceptors (A) are present as A^- anions (I_3^- in the case of iodine)[15,16] with the polymer chain acting as a polycation. At high concentrations the holes delocalize giving rise to metallic behavior.[2] The ionic A^- species evidently reside between the polymer chains and/or the surface of the polymer fibres and thereby lead to increased anisotropy. The

situation may be somewhat analogous to that found in graphite-acceptor intercalation compounds where a dramatic increase in anisotropy is observed after intercalation as a result of insertion of the intercalant between graphite layers.[17] Hsu et al.[15] suggest from their x-ray studies that a similar chain separation effect may be occurring in polyacetylene. This is consistent with the observation that when stretched trans-$(CH)_x$ (l/l_o = 2.36) is doped to give $(CHI_{0.25})_x$ there is no change in length in the direction of alignment, but the transverse dimensions increase by approximately 20% (overall volume change $\sim$ 40%). The density of the doped material (1.26 gm/cm^3) is greater than that of the initial stretched trans-$(CH)_x$ film (0.5 gm/cm^3).

The increase in anisotropy upon doping together with the inferred high conductivity along the polymer chains suggests that we may be dealing with a quasi-one-dimensional (1 d) metallic system in the doped polymer. It will be of interest to direct future experimental studies toward possible observation of the well-known 1 d instabilities.

In summary, partial orientation of the fibers in polycrystalline films of $(CH)_x$ leads to significant improvement in the transport properties and to the introduction of electrical anisotropy. With an elongation $l/l_o \simeq 3$, the room temperature conductivity of AsF_5 doped $(CH)_x$ is in excess of 2000 $(\Omega\text{-cm})^{-1}$, i.e. comparable to that of high quality single crystals of $(SN)_x$. From studies of the temperature dependence we conclude that the

intrinsic $\sigma_{\parallel}$ appropriate to the fully oriented polymer is considerably higher. The increase in anisotropy on doping suggests that at dopant concentrations above the semiconductor-to-metal transition, the metallic state may be quasi-one-dimensional.

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Figure Captions:

Figure 1:

   a.   The electrical anisotropy, $\sigma_\parallel / \sigma_\perp$, as a function of dopant concentration for partially aligned $(CH)_x$ films at different values of elongation (ℓ/ℓ_o)

ℓ/ℓ_o		dopant
▲	2.11	iodine
△	2.11	AsF_5
●	2.91	iodine
○	2.92	AsF_5

   b.   Conductivity of metallic heavily doped $[CH(AsF_5)_{0.10}]_x$ as a function of elongation (ℓ/ℓ_o) as obtained by Montgomery method.

   ● ● ● - parallel to alignment direction
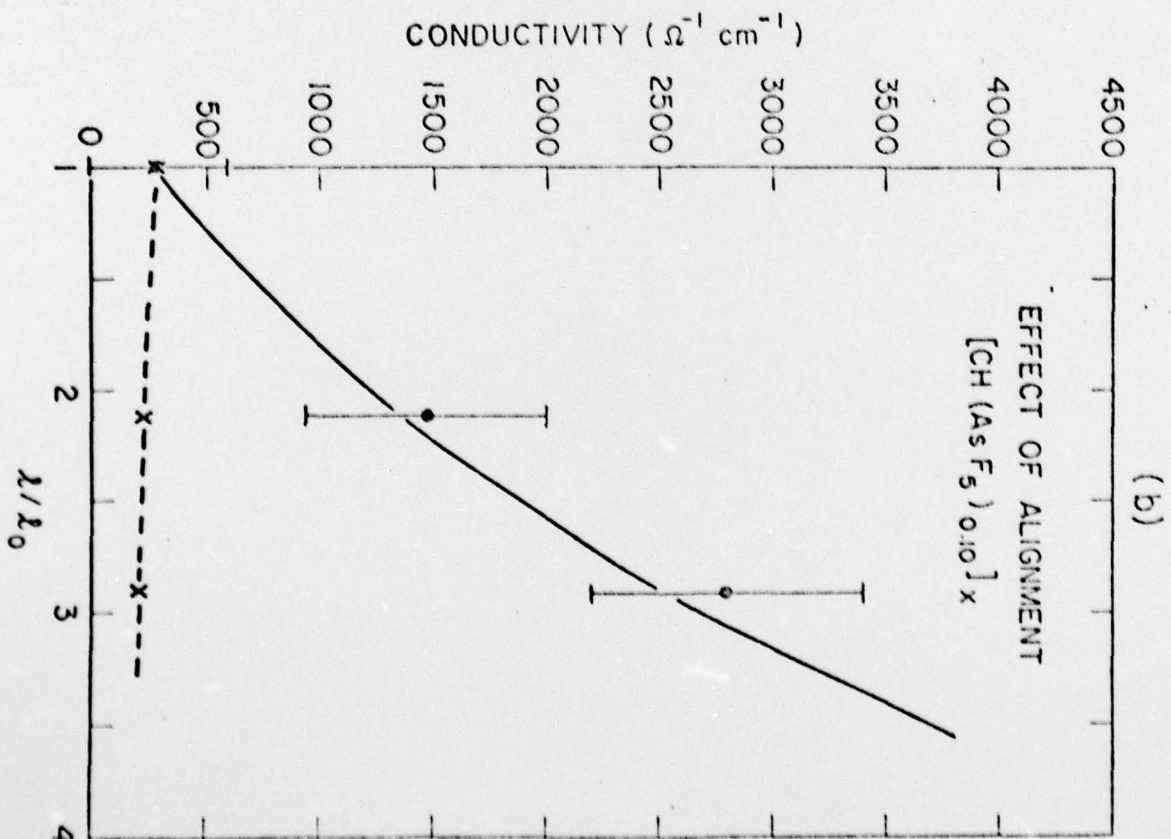   x x x - perpendicular to alignment direction

Figure 2:

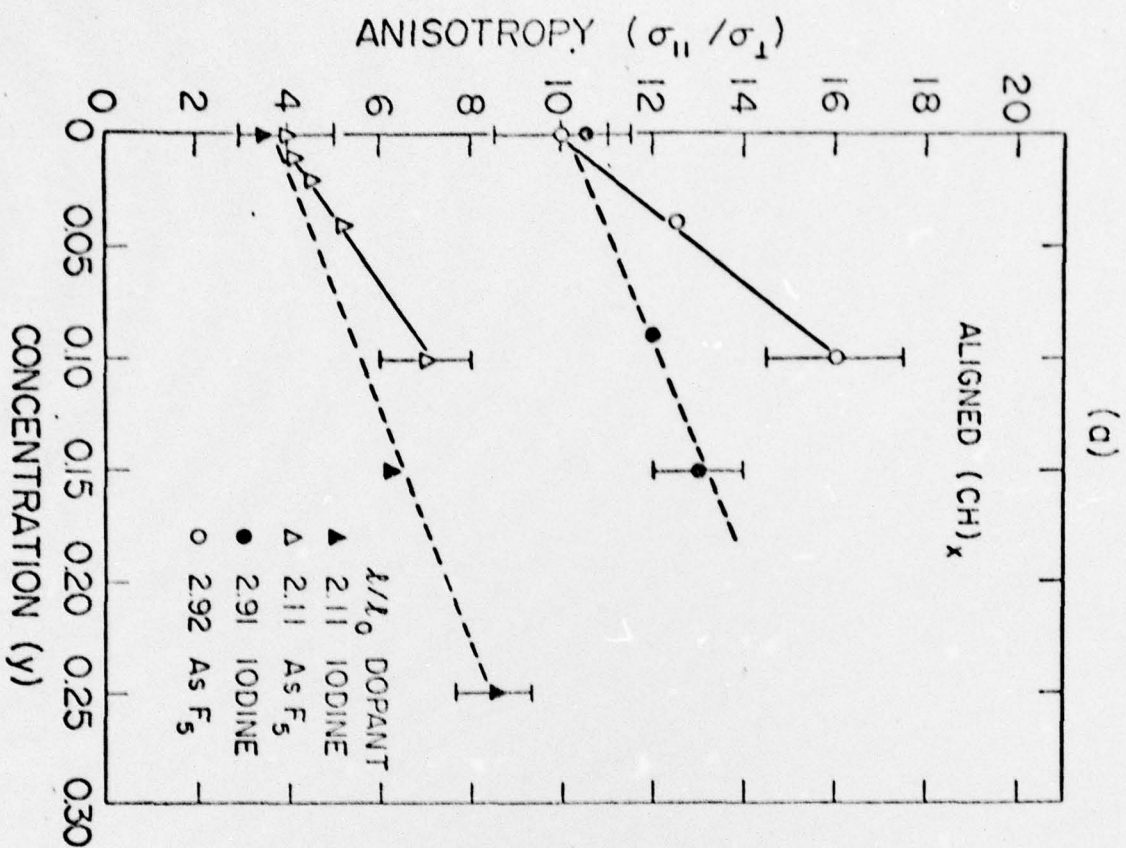   a.   Scanning electron microscope picture of as-grown $(CH)_x$.

   b.   Scanning electron microscope picture of stretch oriented $(CH)_x$.

The average fibril diameter is approximately 200 Å.

Figure 3:   Conductivity versus temperature for oriented $[CH(AsF_5)_{0.10}]_x$. The film was stretch-oriented $(\ell/\ell_o = 2.9)$ prior to doping.

   ● ● ● - four-probe measurements
   x x x - Montgomery measurements

ANISOTROPY ($\sigma_{\parallel}/\sigma_{\perp}$)

0 2 4 6 8 10 12 14 16 18 20

ALIGNED (CH)$_x$

(a)

CONCENTRATION (y)

0 0.05 0.10 0.15 0.20 0.25 0.30

ℓ/ℓ_0 DOPANT
▲ 2.11 IODINE
△ 2.11 As F$_5$
● 2.91 IODINE
○ 2.92 As F$_5$

CONDUCTIVITY (Ω^{-1} cm^{-1})

0 500 1000 1500 2000 2500 3000 3500 4000 4500

EFFECT OF ALIGNMENT
[CH (As F$_5$)$_{0.10}$]$_x$

(b)

ℓ/ℓ_0

0 1 2 3 4
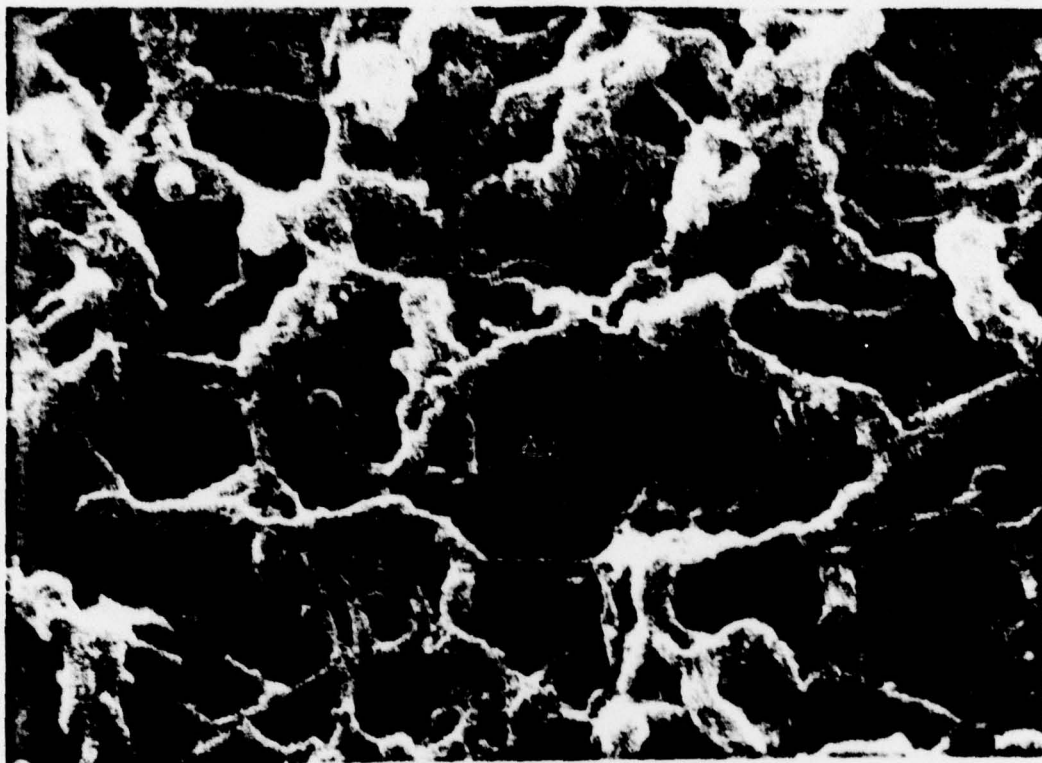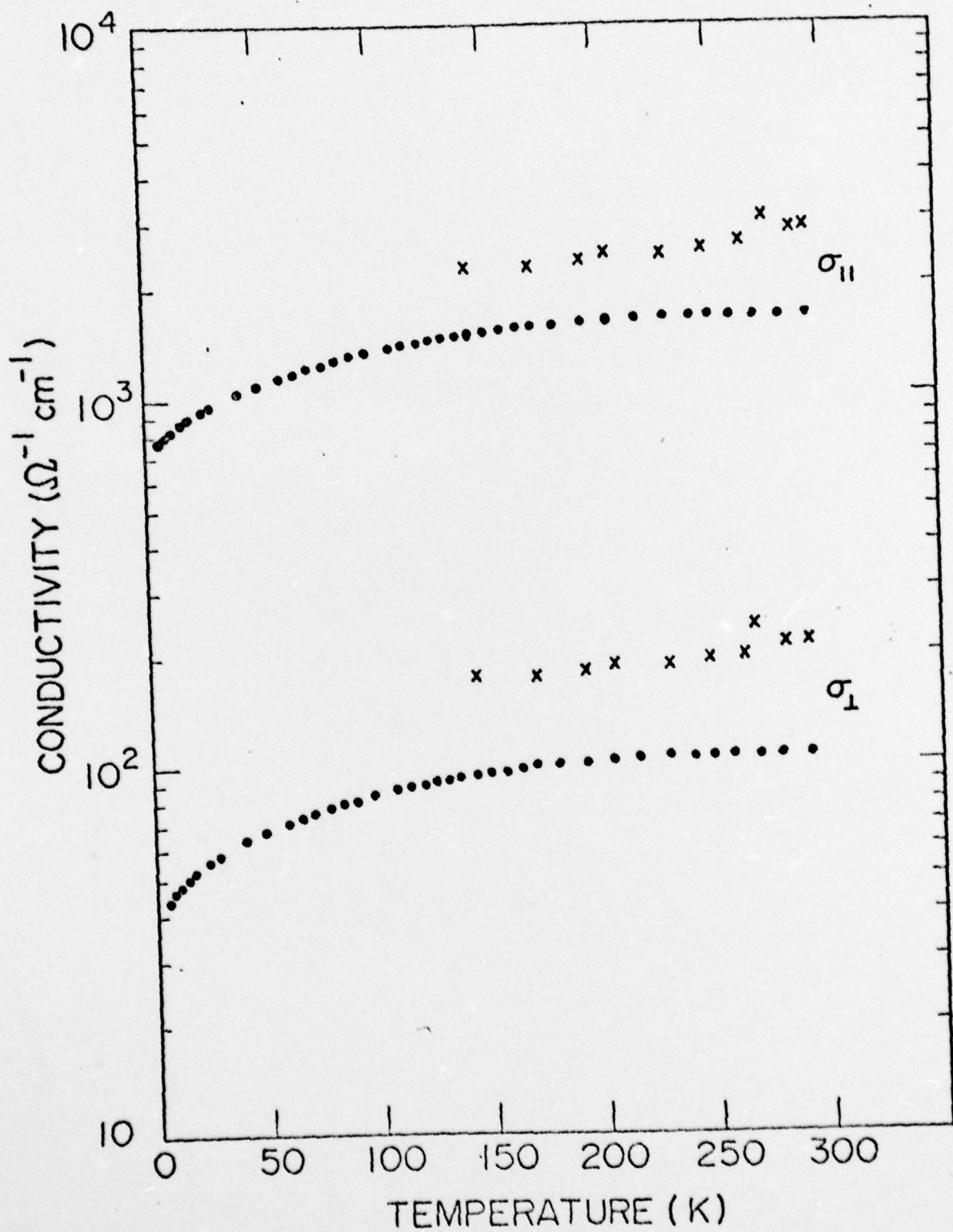
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